Proc. Natl. Acad. Sci. USA
Vol. 78, No. 3, pp. 1323–1326, March 1981
Chemistry

Circulant orbitals for atoms and molecules

(Hartree–Fock method/localized orbitals/density functional theory)

ROBERT G. PARR AND MIN-BO CHEN

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

Contributed by Robert G. Parr, December 1, 1980

ABSTRACT **Circulant orbitals ϕ_n for a closed-shell system are the orbitals obtained when the N canonical orthonormal Hartree–Fock orbitals λ_ℓ are subjected to a unitary transformation which is the discrete Fourier transformation: $\phi_n = 1/\sqrt{N}\,\Sigma_\ell \lambda_\ell \omega^{(n-1)(\ell-1)}$, where $\omega = \exp(2\pi i/N)$. Electron densities associated with the orbitals ϕ_n are each close to the average total electron density. The Fock matrix, diagonal for canonical orbitals, for circulant orbitals is a Hermitian circulant matrix, $\varepsilon_{m,m+q} = 1/N\,\Sigma_\ell \varepsilon_\ell \omega^{q(\ell-1)}$, where the ε_ℓ are the canonical orbital energies. The states $\hat{F}\phi_n$ are uniformly distributed on the surface of a sphere in Hilbert space.**

The invariance of a Hartree–Fock wave function for a closed-shell atomic or molecular system to a unitary transformation of occupied orbitals is well known, and it has been much exploited to define and elucidate spectroscopic (canonical) orbitals on the one hand (1) and localized orbitals on the other (2). Herein is described another such transformation, the transformation to circulant orbitals.

Definition

Consider the Hartree–Fock wave function for a system of $2N$ electrons, the single determinant

$$\Psi = \frac{1}{\sqrt{(2N)!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \cdots & \psi_N(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \cdots & \psi_N(2)\beta(2) \\ \vdots & \vdots & & \vdots \\ \psi_1(2N)\alpha(2N) & \psi_1(2N)\beta(2N) & \cdots & \psi_N(2N)\beta(2N) \end{vmatrix}. \quad [1]$$

The Hartree–Fock orbitals ψ_k are orthonormal, and they satisfy the Hartree–Fock equations,

$$\hat{F}\psi_\ell = \Sigma_k \psi_k \varepsilon^{\psi}_{k\ell}, \quad [2]$$

where the Lagrangian multipliers $\varepsilon^{\psi}_{k\ell}$ are elements of a Hermitian matrix $\boldsymbol{\varepsilon}^{\psi}$. Function 1 is invariant under a unitary transformation of the orbitals ψ_k to new orthonormal orbitals ψ'_m,

$$\psi'_m = \Sigma_k \psi_k U_{km}, \ \mathbf{U}^\dagger\mathbf{U} = 1. \quad [3]$$

The ψ'_m satisfy Hartree–Fock equations

$$\hat{F}\psi'_m = \Sigma_m \psi'_m \varepsilon^{\psi'}_{mn} \quad [4]$$

where

$$\boldsymbol{\varepsilon}^{\psi'} = \mathbf{U}^\dagger \boldsymbol{\varepsilon}^{\psi} \mathbf{U}. \quad [5]$$

The operator $\hat{F}$ is the same in Eqs. 2 and 4.

Canonical or spectroscopic orbitals are orbitals λ_ℓ that diagonalize $\boldsymbol{\varepsilon}$,

$$\hat{F}\lambda_\ell = \lambda_\ell \varepsilon_\ell, \ \langle \lambda_k | \hat{F} | \lambda_\ell \rangle = \delta_{k\ell}\varepsilon_\ell. \quad [6]$$

The "orbital energies" ε_ℓ are excellent approximations to ionization potentials, but for the description of the system of interest there is no inherent reason to prefer the orbitals λ_ℓ to other choices or orbitals. Eqs. 6 determine the λ_ℓ up to arbitrary phase factors in each.

Circulant orbitals are orbitals ϕ_n that are such that the matrix $\boldsymbol{\varepsilon}$ is a Hermitian, circulant matrix—that is, a Hermitian matrix in which every row is a permutation of the one before (3). In terms of a canonical set λ_ℓ, let

$$\phi_n = \frac{1}{\sqrt{N}} \Sigma_\ell \lambda_\ell \omega^{(n-1)(\ell-1)} \quad [7]$$

where

$$\omega = \exp(2\pi i/N) \quad [8]$$

is an Nth root of unity. Then

$$\varepsilon^{\phi}_{mn} = \frac{1}{N} \Sigma_\ell \varepsilon_\ell \omega^{(n-m)(\ell-1)} \quad [9]$$

or

$$\varepsilon^{\phi}_{m,m+q} = \frac{1}{N} \Sigma_\ell \varepsilon_\ell \omega^{q(\ell-1)}. \quad [10]$$

That is, $\boldsymbol{\varepsilon}^{\phi}$ is a circulant matrix. Note that, in general, both the circulant orbitals ϕ and the circulant matrix $\boldsymbol{\varepsilon}^{\phi}$ are complex. The N circulant orbitals are degenerate solutions of one Hartree–Fock equation,

$$\hat{F}\phi_n = \phi_n \bar{\varepsilon} + \sum_{q=1} \phi_{n+q}\, \varepsilon^{\phi}_{n,n+q}. \quad [11]$$

Here, all indices are to be reduced modulo N, and the diagonal elements of $\boldsymbol{\varepsilon}^{\phi}$ have all been set equal to their common value in terms of the canonical orbital energies, the average. For the purposes of the present paper, Eq. 7 defines circulant orbitals.

Examples

As a first example, consider the $1s^2 2s^2$ configuration of atomic Be, with real canonical Hartree–Fock orbitals $(1s)$ and $(2s)$. The total electron density per electron, $\bar{\rho} = 1/2\,[(1s)^2 + (2s)^2]$, differs markedly from the component densities $(1s)^2$ and $(2s)^2$ which describe the "inner" and "outer" parts of the atom, respectively. But the two corresponding circulant orbitals, $\phi_1 = 1/\sqrt{2}\,[(1s) + (2s)]$ and $\phi_2 = 1/\sqrt{2}\,[(1s) - (2s)]$, have electron densities each looking very much like $\bar{\rho}$—namely, $(\phi_1)^2 = \bar{\rho} + (1s)\,(2s)$ and $(\phi_2)^2 = \bar{\rho} - (1s)\,(2s)$. And if one makes the apparently trivial change of including a phase factor i in the second canonical orbital, the two circulant orbitals become

$$\phi_1 = \frac{1}{\sqrt{2}}[(1s) + i\,(2s)],\ \phi_2 = \frac{1}{\sqrt{2}}[(1s) - i\,(2s)], \quad [12]$$

each with precisely the same electron density, $|\phi_1|^2 = |\phi_2|^2 = \bar{\rho}$. No distinction between inner or outer regions of the atom remains.

Second, consider the atom Kr, with electron configuration

$(1s)^2\ (2s)^2\ (2p)^6\ (3s)^2\ (3p)^6\ (3d)^{10}\ (4s)^2\ (4p)^6$. Fig. 1 shows the spherically averaged electron densities $D(\phi_m) \equiv \int \rho_m r^2 d\Omega$ associated with the 18 circulant orbitals obtained by applying transformation 7 to the canonical orbitals. Similarly, Fig. 2 shows the densities for the six circulant orbitals for the $(1s)^2\ (2s)^2\ (2p)^6\ (3s)^2$ configuration of Mg.

The remarkable general features of atomic circulant orbitals are evident from the figures. Their densities vary more or less sinusoidally and not too strongly about the mean total electron density $\bar{\rho}$. Both near the nucleus and far from it their densities become the same, equal to $\bar{\rho}$.

Properties

The most important elementary properties of the circulant orbital transformation are the following, proofs of which are immediate consequences of the fact that the sum of any set of distinct Nth roots of unity is zero.

Property 1. The expectation value of the Hartree–Fock operator is the same for all circulant orbitals, equal to the average $\bar{\varepsilon}$ of the canonical Hartree–Fock orbital energies:

$$\langle \phi_m | \hat{F} | \phi_m \rangle = \frac{1}{N} \Sigma_\ell \varepsilon_\ell = \bar{\varepsilon}. \qquad [13]$$

Property 2. The norm of $\hat{F}\phi_m$ is the same for all circulant orbitals, equal to the average $\overline{\varepsilon^2}$ of the square of the canonical Hartree–Fock orbital energies:

$$\langle \hat{F}\phi_m | \hat{F}\phi_m \rangle = \frac{1}{N} \Sigma_\ell \varepsilon_\ell^2 = \overline{\varepsilon^2}. \qquad [14]$$

Property 3. The mth circulant orbital electron density $\rho_m^\phi = |\phi_m|^2$ is related to the average total electron density $\bar{\rho} = (1/N) \Sigma_m \rho_m^\phi$ by the formula

$$\rho_m^\phi = \bar{\rho} + \frac{2}{N} \sum_{q=1} \left[\cos\left(\frac{2\pi(m-1)q}{N} \right) \mathrm{Re}(\Sigma_k \lambda_k^* \lambda_{k+q}) - \sin\left(\frac{2\pi(m-1)q}{N} \right) \mathrm{Im}\left(\sum_k \lambda_k^* \lambda_{k+q} \right) \right] \qquad [15]$$

Note the oscillatory nature of the correction terms on the right and the unlikelihood that they will be large and negative enough in any given case to produce nodes in the densities ρ_m^ϕ.

Property 4. Define the mean square distance between $\hat{F}\psi_k$ and $\hat{F}\psi_\ell$ by $\Delta_{k\ell}^\psi = \langle (\hat{F}\psi_k - \hat{F}\psi_\ell)|(\hat{F}\psi_k - \hat{F}\psi_\ell) \rangle$ and the mean square distance between all $\hat{F}\psi$ values by

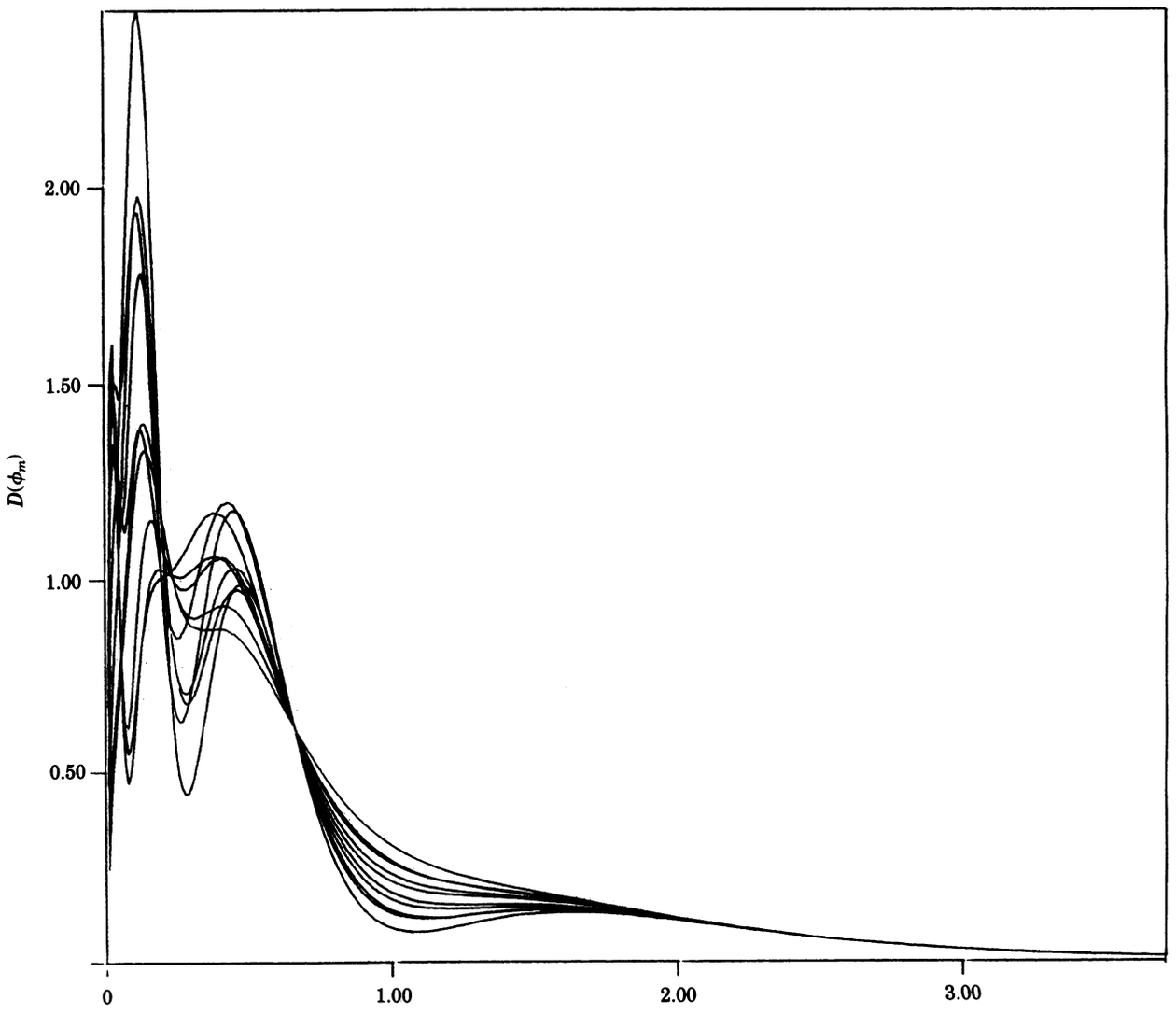

FIG. 1. Spherically averaged densities for the circulant orbitals of krypton, $D(\phi_m) = \int \rho_m r^2 d\Omega$.

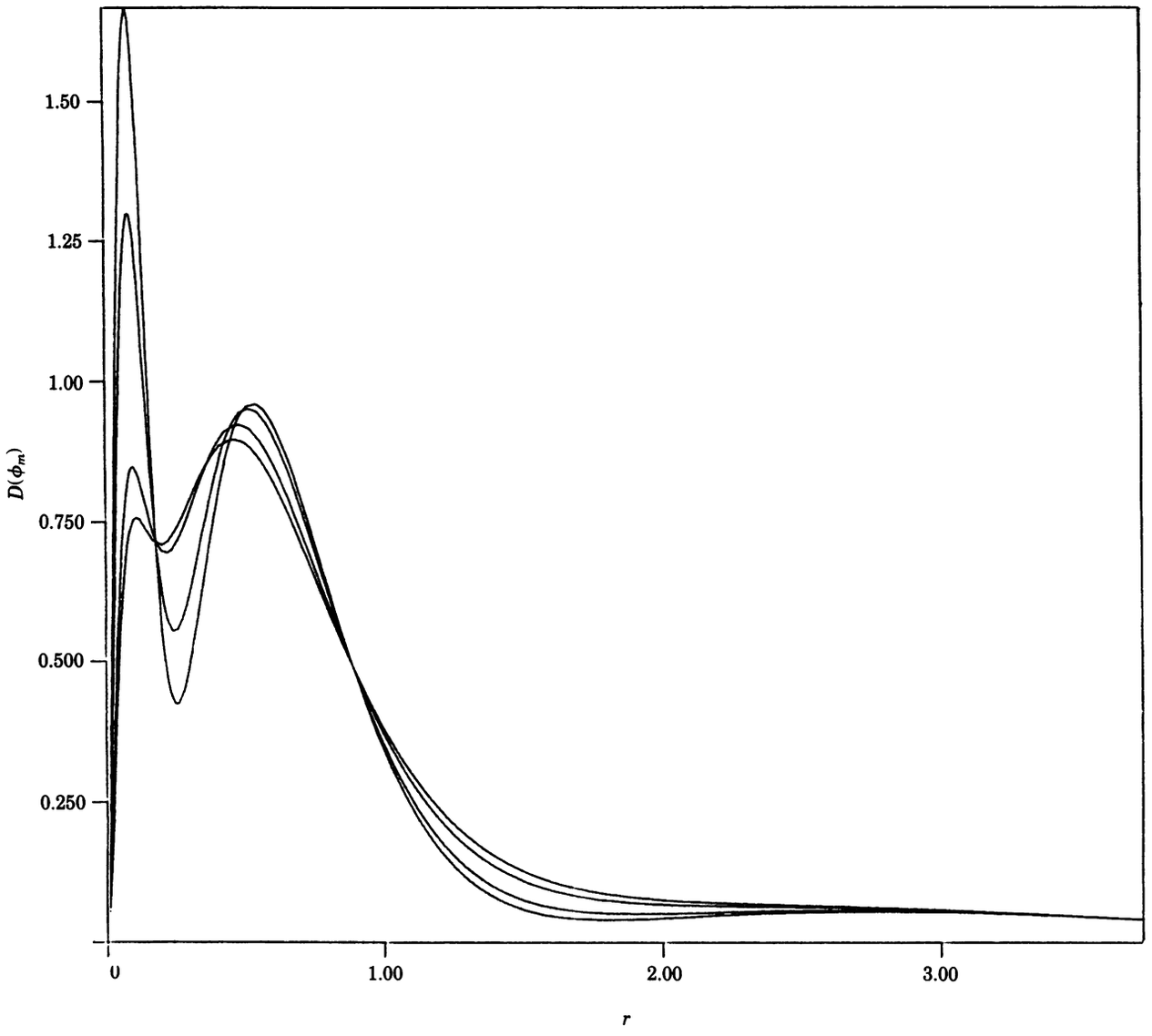

FIG. 2. Spherically averaged densities for the circulant orbitals of magnesium, $D(\phi_m) = \int \rho_m r^2 d\Omega$.

$$\Delta^{\psi} = \frac{2}{N(N-1)} \sum_{k<\ell} \Delta^{\psi}_{k\ell}. \qquad [16]$$

Then, for the circulant orbital set ϕ, the mean square distance is

$$\Delta^{\phi} = \frac{2}{N-1} \sum_{\ell \neq 1} \varepsilon_{\ell}^2 = 2\,\overline{\varepsilon^2}. \qquad [17]$$

That is, Δ^{ϕ} is twice the average of the squares of the canonical Hartree–Fock orbital energies, *leaving out the first*. The corresponding quantity for canonical Hartree–Fock orbitals, Δ^{λ}, has the value $2\overline{\varepsilon^2}$.

Property 4 hints at the most important property of circulant orbitals—that they may always be chosen so as to minimize the average distance between $\hat{F}\phi$ values. Order the canonical orbitals ϕ_k so that the first has the lowest ε_k (highest $|\varepsilon_k|$). Then one has the following theorem:

STATIONARY PRINCIPLE. *The circulant orbitals defined by Eq. 7 minimize the mean square distance* Δ^{ψ} *of* **16**.

In view of **17**, to prove the stationary principle it will be sufficient to prove that

$$\Delta^{\psi} \geq \Delta^{\phi} \qquad [18]$$

for any ψ. To do this, let V be the unitary transformation which takes the canonical set of orbitals λ into the arbitrary set ψ:

$$\psi_k = \Sigma_i \lambda_i V_{ik}. \qquad [19]$$

Then

$$\begin{aligned} \Delta^{\psi}_{k\ell} &= \langle (\Sigma_i (V_{ik} - V_{i\ell})\varepsilon_i \lambda_i) | (\Sigma_i (V_{ik} - V_{i\ell})\varepsilon_i \lambda_i) \rangle \\ &= \Sigma_i [|V_{ik}|^2 + |V_{i\ell}|^2 - 2\mathrm{Re}(V^*_{ik} V_{i\ell})]\varepsilon_i^2, \end{aligned} \qquad [20]$$

so that

$$\Delta^{\psi} = \frac{2}{N} \Sigma_i\, \varepsilon_i^2 - \frac{4}{N(N-1)} \sum_{k<\ell} \Sigma_i\, \mathrm{Re}(V^*_{ik} V_{i\ell})\, \varepsilon_i^2. \qquad [21]$$

By using first

$$V^*_{1k} V_{1\ell} = -\sum_{i \neq 1} V^*_{ik} V_{i\ell} + \delta_{k\ell} \qquad [22]$$

and then

$$0 \leq |\Sigma_k V_{ik}|^2 = 1 + 2 \sum_{k<\ell} \mathrm{Re}(V^*_{ik} V_{i\ell}), \qquad [23]$$

there now results

$$\Delta^{\psi} = \frac{2}{N}\Sigma_i\,\varepsilon_i^2 + \frac{4}{N(N-1)}\sum_{k<\ell}\Sigma_i\,\mathrm{Re}(V_{ik}^{*}V_{i\ell})(\varepsilon_1^2-\varepsilon_i^2)$$

$$= \Delta^{\phi} + \frac{2}{N(N-1)}\Sigma_i\left[1+2\sum_{k<\ell}\mathrm{Re}(V_{ik}^{*}V_{i\ell})\right](\varepsilon_1^2-\varepsilon_i^2) \quad [24]$$

$$\geq \Delta^{\phi}$$

which is the desired result.

DISCUSSION

England and Ruedenberg (4) have already pointed out that some (and, by implication, all) of the diagonal elements in an ε matrix could be made equal, and they used the term "homogeneous localization" to describe the family of such orbital transformations. Within this family, the present work considers the unique discrete Fourier transformations defined by Eq. **7**. The structure of the Fock matrix which results demands the name "circulant orbitals" for the resulting orbitals.

Circulant orbitals have densities each everywhere close to the average total electron density and in that sense are highly delocalized. More quantitatively, the properties manifest in Eqs. **11**, **13**, **14**, **15**, and especially **18** mean that circulant orbitals are as similar as possible to each other in the sense measured by the quantities $\hat{F}\phi_n$ and the distances between them. The states $\hat{F}\phi_n$ have the remarkable property that they are uniformly distributed on the surface of a sphere of radius $(\overline{\varepsilon^2})^{1/2}$ in Hilbert space.

The present work implies that searches for localized orbitals in atoms and molecules (2) should no longer be restricted to searches for real orbitals. Circulant orbitals themselves should be extremely useful in studying the transition between and relations among orbital theories and density functional theories of electronic structure of atoms and molecules (5, 6).

This research has been aided by grants to the University of North Carolina from the National Science Foundation and the National Institutes of Health.

1. Koopmans, T. (1933) *Physica* **1**, 104–113.
2. Edmiston, C. & Ruedenberg, K. (1963) *Rev. Modern Phys.* **35**, 457–465.
3. Davis, P. J. (1979) *Circulant Matrices* (Wiley, New York).
4. England, W. & Ruedenberg, K. (1973) *J. Am. Chem. Soc.* **95**, 8769–8775.
5. Hohenberg, P. & Kohn, W. (1964) *Phys. Rev. B*. **136**, 864–871.
6. Donnelly, R. A. & Parr, R. G. (1978) *J. Chem. Phys.* **69**, 4431–4439.